



Path analysis on CO₂ resource utilization based on carbon capture using ammonia method in coal-fired power Plants

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ABSTRACT

With the deepening of carbon capture research using ammonia solution, CO₂ disposal problem after carbon capture has become an important limiting factor affecting the industrial applications of carbon capture technology. It can be seen that CO₂ not only controls as a greenhouse gas, but also it is a valuable carbon resource at the same time, CO₂ resource recycling has a very good market prospects in near future. Two viable paths for CO₂ resource utilization based on carbon capture using ammonia solution are divided in the paper. One path is regenerative resource utilization, i.e., rich liquid regenerates after the decarbonization reaction; the desorbed CO₂ is sequestered under geological layer or reused in other fields. Another path is transformed resource utilization; flue gas decarbonization combines with chemical production, and the ingredients produced from the reaction of ammonia with CO₂ are transformed, carbon is fixed into nitrogen fertilizer or other chemical products, such as soda. The existing problems and the economic performance of CO₂ resource utilization in power plants were reviewed in the paper. CO₂ resource utilization based on carbon capture using ammonia solution is beneficial to the carbon emission reduction in coal-fired power plants; especially transformed resource utilization has economic advantage and good application prospects.

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1. Introduction

Shaun et al. from U.S. published a research report in *Science*, said that over the past decade, the average global temperature was higher than that of more than 80% particular years in the past 11,300 years. Over the last 100 years or so, the temperature increased significantly, which was consistent with the increasing trend of atmospheric CO₂ concentration after industrial revolution, the fact proved that global warming was a result of human activities [1]. According to data released by the Economic Cooperation and Development (OECD) and the International Energy Agency (IEA), about 10.6 billion tons CO₂ was discharged from the existing power plants, accounting for 40.6% of the total CO₂ emissions worldwide, among these coal-fired power plants CO₂ of 7.6 billion tons was emitted, accounting for 72% of the total emissions in the power generation industry [2]. For example, coal accounted for more than 65% of the primary energy production and consumption in China, CO₂ emissions from thermal power plants kept at about 60% of the total emissions [3,4]. Therefore, Carbon Capture Utilization and Sequestration (CCUS) for the power plants is more feasible measure to slow down CO₂ emission in the near future [5].

Flue gas post-combustion CO₂ capture in coal-fired power plants consists of absorption, adsorption, membrane separation, chilling ammonia, etc. Considered with CO₂ in flue gas with low partial pressure, huge gas flow rate as well as complex co-existing components in flue gas, the chemical absorption method is a more appropriate choice compared with other methods [6]. In the chemical absorption method, the most serious concern is alcohol amine method, in which monoethanolamine (MEA) is used most extensively, but its CO₂ absorption efficiency is not high, the regeneration product is only CO₂, and due to oxidation, thermal degradation, irreversible reactions and heat evaporation causes the loss of absorbing capacity, degradation products from rich CO₂ absorption solution (referred to as the rich liquid) cause system corrosion, furthermore, energy consumption in generation process, the initial investment and the operation cost are all high [7]. In order to solve these problems, in recent years, researchers have proposed carbon capture using ammonia solution to replace the traditional MEA absorption [7,8]. Then, the technical and economic feasibilities on CO₂ removal using ammonia solution have been explored by many researchers and research institutions, the results indicate that minimizing the decrease of power plant production efficiency can be achieved through the multi-pollutants control in power plants using ammonia solution [9].

With the in-depth research, researchers realized that CO₂ was a valuable carbon resource, the possibility of its resource recycling should be considered simultaneously, therefore carbon capture using ammonia method should think over not only the reduction of CO₂ emission, but also the dispose of CO₂ after decarbonization [10]. Two feasible resource path based on CO₂ capture using

ammonia solution (ammonia decarbonization) were divided in the paper, as shown in Fig. 1. One path is regenerative resource utilization: the rich liquid is regenerated after decarbonization, regeneration method consists of conventional heating regeneration and regeneration through ion exchange resin [8,11–16], then the desorbed CO₂ is sequestered or used in other fields; another path is transformed resource utilization which combines the flue gas decarbonization with chemical production, the products after the CO₂ capture using ammonia solutions transform and fix into nitrogen fertilizer or other chemicals [17–20].

In view of the results of previous studies, a review about the paths of CO₂ resource utilization based on CO₂ capture using ammonia solution was carried out, related mechanisms, application prospect and economic aspect were investigated, existing problems and further development direction were also given, and the research could provide valuable contribution to the future development of carbon emission reduction.

2. The paths of CO₂ resource utilization

2.1. CO₂ capture using ammonia solution

2.1.1. Mechanism and progress of CO₂ capture using ammonia solution

CO₂ capture using ammonia solution could be traced back to 1997, Bai et al. [8] used ammonia solution to capture CO₂ from flue gas in power plants, and the studies on factors affecting CO₂ removal efficiency and absorption capacity were carried out in a semi-continuous bubbling absorption device [21]. Since then, the bubbling reactor, stirred tank, packed tower, sieve column, over-weight bed and other equipment were applied for studying the CO₂ capture using ammonia solution, many relevant lab data were obtained [15,22–29]; in addition, Aspen Plus software was used to simulate and evaluate the technical and economic feasibility of flue gas CO₂ capture using ammonia solution in power plants [17,30,31], the results could improve the design of the carbon capture process. With further researches, CO₂ capture using ammonia solution attracted more and more attention, experimental study of ammonia carbon capture was carried out, and the results of infrared spectroscopy showed that the main content of solution was NH₄HCO₃ [24,32]. According to recent researches, for the solubility limit of NH₄HCO₃, the regeneration ammonia decarbonization technology without crystal in low concentration condition should apply ammonia solution with concentration less than 2 mol/L, and with the mass fraction of 2%, removal efficiency of CO₂ could be more than 90% [33,34]. But the high concentration ammonia solution can lead to ammonia escape and crystallization causing clog, which must be solved towards the industrial application while the crystal is the base of regenerative resource utilization and transformed resource utilization [35,36].

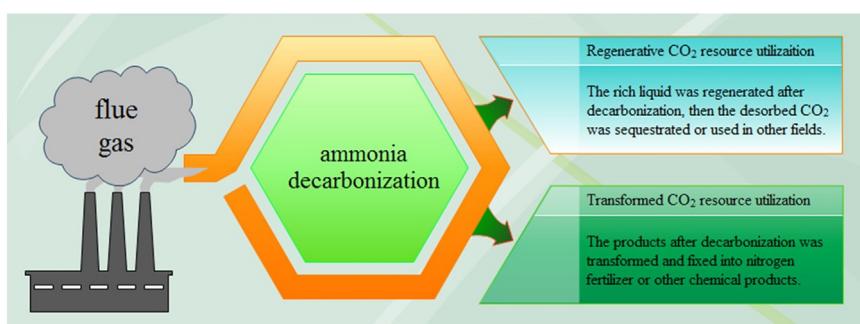
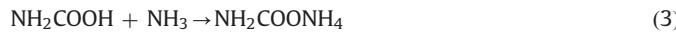


Fig. 1. Two feasible resource paths based CO₂ capture using ammonia solution in power plants.

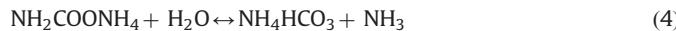
CO₂ capture using ammonia solution accomplishes through reversible chemical reaction. Referred to the two-film theory, liquid film constitutes the predominant mass transfer resistance [24], so the key to improve absorption is the liquid film resistance. The main reaction mechanism is as follows:



Actual reaction process is more complex with a series of intermediate stages. The reactions are as follows:



Hydrolysis of NH₂COONH₄:



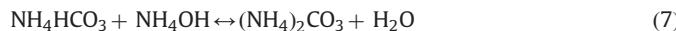
NH₄CO₃ is generated by absorbing CO₂:



At the same time, NH₄OH is generated:



(NH₄)₂CO₃ can be generated by reversible reaction of NH₄HCO₃ and NH₄OH:



The formation of ammonium carbamate (2) and (3) are secondary, rapid and irreversible reactions [37,38], which primarily occur in the liquid film; the hydrolysis of ammonium carbamate (4) is a relatively slow reaction [39]. During the ammonia decarbonization, molecules of CO₂, H₂O, NH₃, O₂, H₂CO₃, etc. and ions of NH₄⁺, H⁺, OH⁻, NH₂COO⁻, HCO₃⁻, CO₃²⁻, etc. may exist in the solution [40,41]. Among these ions, it is notable that the content of CO₃²⁻ is always much less than that of NH₂COO⁻, HCO₃⁻ [42]. Therefore majority of desorption studies were based on NH₂COO⁻ and HCO₃⁻. In process the concentration of production varies with reactant and the carbonization: carbonates or bicarbonates in dilute aqueous ammonia; carbamate in concentrated aqueous ammonia [43]. After decarbonization the concentration of ammonia solution decreases, so NH₄HCO₃ is mainly formed, which produces two utilization paths of regeneration and transformation.

2.1.2. The existed problem of ammonia decarbonization

For ammonia decarbonization, most researches were aimed at non-continuous, microscopic mechanism, the researches for macro kinetics of the reactor design and related practical mathematical model were few while they were essential for the actual design, materials measure and materials balance collapse caused by ammonia escape are the main reasons [44–47]. In addition, due to the high saturated vapor pressure and the fast evaporation rate, ammonia escape is an important technical issue, which caused secondary pollution, corrosion and materials loss which brake the material balance while there are no effective methods to recover ammonia in the lab [48,49]. The common solutions are multi-stage washing device installed at the top of the absorber and additional washing tower to remove escaping ammonia, but these methods also affected the water balance and energy consumption in the process [50]. Some lab researches were done to control the ammonia escape in a certain range, ions and organism were added into ammonia solution to control free ammonia, but there were few studies in industrial scale and conditions [51–57]. At present SCR/SNCR using ammonia and the ammonia desulfurization in power plants are applied [58,59]. Meanwhile ammonia solution can be used for CO₂ capture, therefore ammonia can be used for the removals of SO₂, NO_x, and CO₂, but the ammonia escape also occurs in denitrification and desulfurization with ammonia solution.

2.2. Regenerative resource utilization

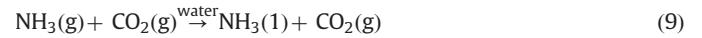
2.2.1. Mechanism and progress of regenerative resource utilization

The path is made up of two parts, desorption and CO₂ resource utilization, where the product is industrial CO₂. The core is desorption of NH₄HCO₃ generated by ammonia decarbonization, the main reactions are shown as follows:

NH₄HCO₃ is decomposed by heating:



The mixed gas containing CO₂ and NH₃ is separated by water washing:



After decarbonization the absorbing liquid is heated in the regeneration tower (8), then the mixed gas containing CO₂ and volatile ammonia is separated (9). NH₃ is recycled for ammonia decarbonization, CO₂ is disposed such as sequestration or sale. It is the perfect theoretical cycle with no ammonia loss while ammonia escape problem is serious in practice.

The researches for regeneration mainly focused on desorption of solution containing NH₄HCO₃ and (NH₄)₂CO₃ [8,27,29]. For traditional thermal regeneration, semi-continuous heating test was carried out in the solution containing NH₄HCO₃ and (NH₄)₂CO₃, results showed that, with the increasing concentration of HCO₃⁻ and the increasing regeneration temperature, desorption rate of CO₂ increased, which was beneficial to the cycle of regeneration [18,22,60,61]. But higher the temperature, higher the heating and separation energy consumption, which must be considered in practice.

Based on the Electro-Catalytic Oxidation (ECO), the ECO₂ technology removing CO₂ combined with desulfurization and denitrification, as shown in Fig. 2(a), developed by the Powerspan Ltd. US, uses the ammonia solution to absorb CO₂. CO₂ removal efficiency can be reach to 90% at the temperature of 54 °C and reaction time of 4–5 s. Then the rich liquid is regenerated and utilized. Its material transformation is shown in Fig. 2(b) where only ammonia solution is inputted as raw material, the energy is mainly inputted in regeneration of ammonia solution and separation of CO₂. The relevant demonstration projects of 20 t CO₂/d was built at First Energy's R.E. Burger Plant, USA, and operated in 2008, the process performance and the economic status were evaluated. The evaluation showed that the technology had good environmental and economic benefits [29,62]. ECO₂ technology is a typical regeneration path, after CO₂ adsorption, the rich liquid is pumped to the heat exchanger (exchange between rich liquid and poor liquid), then to the regeneration tower to separate CO₂ and regenerate ammonia solution used to next cycling. But the ammonia escape is still not solved and because of the technological problem and system stability, it is still a long distance towards wide application.

2.2.2. Applications and existing problems of regenerative resource utilization

According to theoretical analysis and system simulation, energy consumption of CO₂ capture using ammonia solution was expected to be about 40% of MEA method, and by heat integrated management about extra 25% of the energy consumption could be saved, and the energy consumption of CO₂ capture using ammonia solution was estimated to be 0.04–0.09 MW h/t CO₂ [9,22,63]. In accordance with the researches, the energy consumption of MEA method was 0.19–0.38 MW h/t CO₂, equivalent to 20–30% of the typical units output; the energy consumption for thermal regeneration of CO₂ accounted for 50% of all, which was much higher than that of ammonia decarbonization [29]. Whether

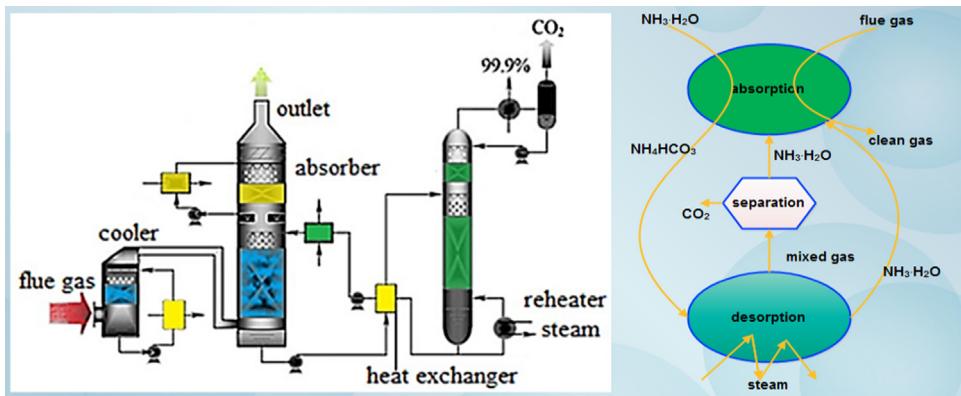


Fig. 2. The process and material transformation of ECO₂.

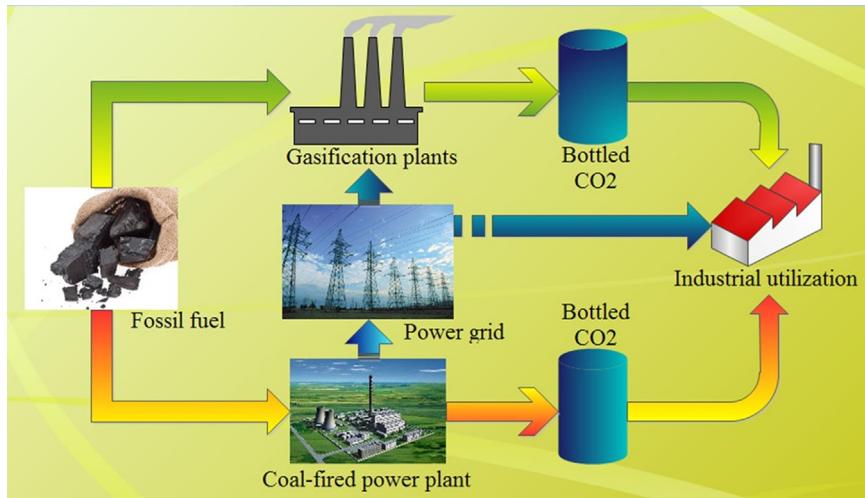


Fig. 3. Relationship of regenerative CO₂ resource utilization and traditional industrial CO₂ utilization.

ammonia or MEA, the cost of carbon capture is too huge for power plants at present without policy supports.

The industrial CO₂ purity of 99.9%, which is used for food industry, chemical industry, machine industry, etc., can be produced by the ECO₂, and it provides an impressive revenue for enterprises [28,64–66]. Utilization through the market is one of main ways of CO₂ resource utilization, but the market saturation of CO₂ will come true in the future, therefore the rest CO₂ need to find disposal methods such as biological technology, sequestration, etc. Among sequestration technologies, the geological sequestration attracts the most attention, secondly the ocean sequestration, etc. [67–69]. Compared with other sequestration technologies, geological sequestration is the most feasible in aspects of economy and environment. EOR (Enhanced oil recovery technology) and EGR (Extreme pressure gas recovery technology) are not only profitable, but also environment friendly in theory, and therefore more and more emphasis is put on them [70,71]. According to the studies, geological sequestration have a huge potential capacity, in China the capacity is expected to reach more than 2000 Gt CO₂, while there are many difficulties in its application, mainly the investment and low profit [72–74].

The designed relationship of regenerative CO₂ resource utilization and traditional industrial CO₂ utilization is shown in Fig. 3. Power generation and production of bottled CO₂ are accomplished in the power plants in the same time, and the bottled CO₂ is provided for industry to achieve the utilization of CO₂ while traditional industrial CO₂ utilization mainly relied on gasification plants [75]. Theoretically apart from CO₂ production from gasification plants are replaced by CO₂ recycled in power plants, therefore,

CO₂ emission from human activities and exploitation of fossil fuel has reduced; and without the power transportation from power plants to gasification plants, the line loss can be reduced and the efficiency can be improved, which are important for enterprises. This is a possibility based on the developed transformed technology in the power plants.

As for the entire regenerative CO₂ resource utilization, alkalinity of absorbent after thermal regeneration becomes weaker, so some methods are essential to improve the efficiency of cycling decarbonization and regeneration ratio of ammonia. After the CO₂ regeneration, geological sequestration of CO₂ faces many problems, such as low reliability, high investment, and high energy consumption [71,76–79]. Compared with huge CO₂ discharge from power plants, the reduction of CO₂ can hardly be achieved through the regenerative resource utilization or transformed resource utilization, and finally it still needs the sequestration technology. But the sequestration is limited by existing problems, low economic compensatory, environmental risks, etc., for example, monitoring data of Salah CO₂ sequestration project showed that annual rising height of land surface reached 5 mm [80,81]. The promotion of sequestration technology faces many obstructions and controversies, therein the potential risk of leakage cannot be ignored [82–84].

2.3. Transformed resource utilization

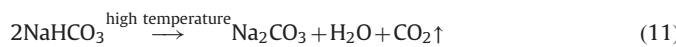
2.3.1. Mechanism and progress of transformed resource utilization

Relevant literatures showed that the idea of decarbonization in the flue gas using ammonia solution was derived from the process,

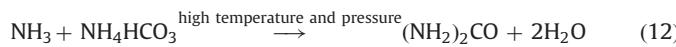
which produced ammonium bicarbonate with the Haber process, put forward by Hou [85,86] in China, 1958. Chemical production after CO_2 capture using ammonia solution is a CO_2 resource utilization combined with the Hou's process for soda production, and the core of the transformed resource utilization is the chemical production. But because of differences in conditions such as high flow rate and high temperature, flue gas containing a large number of inert gas N_2 , as well as O_2 , SO_2 , NO_x , heavy metals, and particulate matter, CO_2 capture using ammonia solution in power plants is different with traditional methods. Many studies of decarbonization using ammonia solution were carried out [87]. Liu et al. [23] and Zhang et al. [29] recommended the ammonia concentration of 10% for carbon capture considering operation cost and secondary pollution; Yeh et al. [21] recommended the ammonia concentration of 28% as CO_2 absorbent through experimental studies; considered from the industrial application of pressing decarbonization, Corti et al [17] came up with the ammonia concentration of 3.4%; according to the related researches, in the continuous decarbonization process, while the increasing concentration of CO_2 could improve the removal efficiency, the ammonia escape should be emphasized [27,28,87]; related researches about temperature showed that the reaction temperature is generally in 10–40 °C, but the practical temperature should be decided based on tower type, costs and heat exchange capacity [21,27,28]; Operation conditions of ordinary pressure have been proposed by researchers to apply in the production of ammonium bicarbonate, which is beneficial to the energy consumption [88].

In according to the existing instance and studies, byproduct could be obtained based on the absorption process in the low concentration of CO_2 , i.e. chemical production of substance after decarbonization where CO_2 was transformed into chemicals [89]. What is different from regeneration path through MEA? Transformed path through ammonia method can derive different chemical products to the fixed CO_2 with the reaction production NH_4HCO_3 .

Theoretically there are a lot of possible transformed path with NH_4HCO_3 solution after ammonia decarbonization, related reactions are as follows:



In addition, after the appropriate amount of ammonia is injected to the NH_4HCO_3 solution, urea can be produced with heating and at elevated pressure:



So long as the absorption of CO_2 in the low concentration is not solved, the next step of alkali process cannot come true. But in the researches of CO_2 capture using ammonia solution at present, CO_2 could be absorbed in the low concentration and the liquid containing NH_4HCO_3 could be obtained. Learned from the Hou's process [43] for soda production, NaCl was added into carbonation solution, and the substance could be separated based on the difference of solubility. After centrifugation, filtration, and drying, NaHCO_3 could be obtained according to Eq. (10), and Na_2CO_3 could be obtained by heating decomposition of NaHCO_3 from Eq. (11).

Such transformed processes is applied widely in chemical plants using Solvay process, but the researches based on the low concentration CO_2 in power plant were absent, and most of them were focussed on the theoretical researches [90]. Related experimental studies were mainly carried out in chemical plants, Liao et al. [91] studied with dry salt phase diagram (shown in Fig. 4), and details listed as follows:

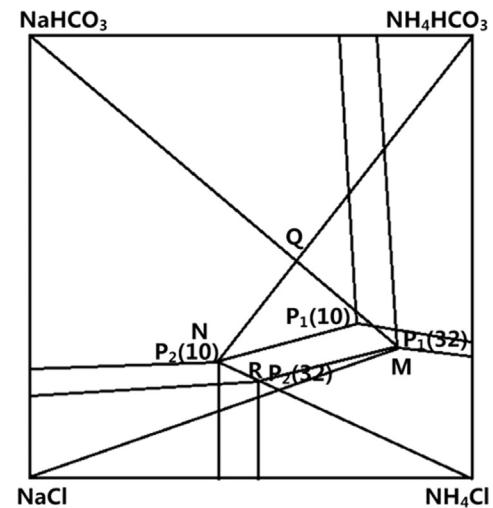


Fig. 4. Dry salt phase diagram.

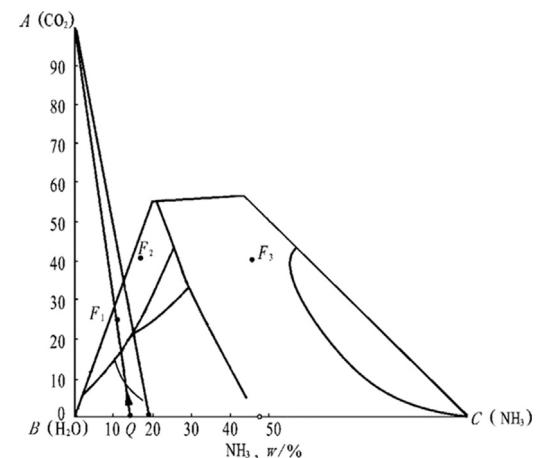


Fig. 5. $\text{NH}_3\text{--CO}_2\text{--H}_2\text{O}$ ternary liquid-solid equilibrium phase diagram.

- 1) The mother liquor is heated to 32 °C to separate out NaHCO_3 (the equilibrium point $P_1(32)$, namely point M);
- 2) NaCl is added into the mother liquor, the equilibrium point move to $P_2(32)$, namely R, where is the NH_4Cl phase area;
- 3) The mother liquor is cooled to 10 °C to separate out NH_4Cl (the equilibrium point $P_2(10)$, namely point N);
- 4) The mother liquor is heated to 32 °C to move the equilibrium point to Q, and then NaHCO_3 is added into the mother liquor to move the equilibrium point to M.

Liao et al. [91] considered that the cycle of MRNQM in Fig. 4 can be used to achieve the reaction (10) and it is possible to produce NaHCO_3 and Na_2CO_3 with the mother liquor containing NH_4HCO_3 after ammonia decarbonization. The cycle is common in chemical plants while it provided a possible way for transformed utilization of carbon capture using ammonia solution. The waste heat of plants is used for heating and pressing, while the cooling process in the cycle can be a problem related electric power requirement.

Some researchers raised an idea to produce NH_4HCO_3 by using ammonia to capture CO_2 from flue gas, then NH_4HCO_3 was used as fertilizer to fix CO_2 in the soil [26,19]. This is not only a path of CO_2 resource utilization from flue gas, but also a method with economic benefits. Based on Janecke's research, thermodynamic analysis was carried out by Shen et al. [92] based on $\text{NH}_3\text{--CO}_2\text{--H}_2\text{O}$ ternary-liquid-solid equilibrium phase diagram (shown in Fig. 5). The material points F_1 and F_2 are located in the NH_4HCO_3

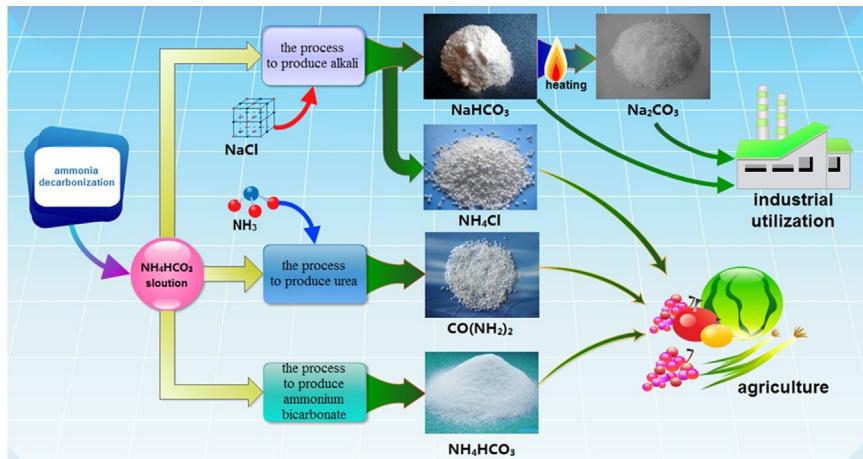


Fig. 6. The process of transformed CO₂ resource utilization.

phase area, then the reactor is cooled and NH₄HCO₃ solid can be obtained. Material point F_3 is located in the NH₂COONH₄ phase area, only the solid ammonium salt can be obtained by cooling. Therefore, in order to produce NH₄HCO₃ the total material point (referring to the matching of NH₃, CO₂, and H₂O) must be set in the NH₄HCO₃ phase area, such as F_1 or F_2 . Though these material points could be achieved in chemical plants easily, when the method is used in power plants the control of the materials in the solution after ammonia decarbonization would be very necessary.

As seen in Fig. 5, in order to obtain the pure crystallization of NH₄HCO₃, the carbonation process must be operated without the (NH₄)₂CO₃·H₂O phase area (the left of line AE, such as points F_1). For example line QA, started at point Q, and the carbonation process is operated along with line QA, from Q to A related the saturation process of CO₂ in solution, finally NH₄HCO₃ is separated out. When the raw materials point is located in the right of line AE with the too high NH₃ concentration (F_2), other salt appeared during the carbonation process and the product is not pure NH₄HCO₃. As long as the raw materials point is set in the certain phase area, it is possible to produce NH₄HCO₃ with CO₂ in flue gas. Related calculation was achieved by scholars, calculation was started at w(NH₃) ≈ 12.2% w(CO₂) ≈ 10.96% and result, total composition point, was located in NH₄HCO₃ area, NH₄HCO₃ solid and the corresponding suspension solution (mother liquor) could be obtained at 20–50 °C suspension, which also adjusted to the operating temperature of ammonia decarbonization [92]. But the difficulties are obvious, the cool system and accurate material control methods must be researched and developed firstly.

A method to produce urea with ammonium bicarbonate solution was disclosed in Chinese patent [93]. Mother liquor containing ammonium bicarbonate is used as the raw material, and reaction (12) occurred at the temperature of 100–280 °C, the pressure of 4.0–25.0 MPa, the molar ratio of ammonia to carbonate ammonium hydrogen of 1–10, the molar ratio of water to ammonium bicarbonate of 0–15, the reaction time of 0.5–2 h. But the method is mainly applied on nitrogenous fertilizer plants. When the related method is applied in coal-fired power plant, the purchase of CO₂ is leaved out while some adaptive improvements, such as the control of NH₄HCO₃ concentration in the mother liquor, reduction the reaction time, were needed.

2.3.2. Application and existing problems of transformed resource utilization

The carbonate and bicarbonate production after CO₂ capture have been studied, but lack of studies related the derivate [94]. Although the transformed CO₂ resource utilization is different

from other carbonation production in the process, their goals were the same. Transformed CO₂ resource utilization is shown briefly in Fig. 6, after the CO₂ capture using ammonia solution NH₄HCO₃ solution enters the process to produce alkali, urea and ammonium bicarbonate, and the products are NaHCO₃, Na₂CO₃, NH₄Cl, CO(NH₂)₂, NH₄HCO₃ respectively. The by-products, NH₄HCO₃, CO(NH₂)₂ and NH₄Cl, are available as the agricultural fertilizers with certain economic benefits [19].

As seen in Fig. 6, the productions are consumed by agriculture and industry eventually. With biological sequestration in agriculture, carbon is absorbed and utilized by plants and converted into organic matter; a part of the industrial market capacity is replaced by the production of NaHCO₃, Na₂CO₃ from CO₂ utilization in power plants, in other words it can reduce the CO₂ emission from fossil energy and carbon-containing minerals. Considered as the raw materials, the liquor containing of NH₄HCO₃ have more available derivatives than solution from carbon capture using MEA. Compared to regeneration utilization, transformed resource utilization using ammonia solution is lack of related study because majority of carbon capture focused only one part of carbon capture system or insulated itself from other industry.

But before its application, there are many unsolved problems to be researched and solved. The application of chemical production in the power plant is influenced by many factors which are lack of development such as the reaction condition, mechanism, kinetics, energy consumption, etc. [86]. The advantage of energy consumption is the key to the application of chemical production in the power plants, but researches in this area are rarely done. And the performance of utilization production also needed to meet the market requirements in order to be accepted by the market, it is very important to research it associated with market economy.

3. Economic analysis of CO₂ resource utilization in power plants

Compared with the global CO₂ emission from human activities, the demand amount of CO₂ in the social production is much smaller [2,94], therefore the utilization of carbon reduction in its infancy ought to be considered and achieved firstly, and then the CO₂ sequestration. As a path of CO₂ resource utilization with economic attractiveness combining the carbon capture with profitable production, it is most likely to achieve the best economic goal. More importantly the best economic balance between the carbon emissions and carbon capture could be achieved, while the pure carbon capture is questionable to be verified not only on the economic but also on environmental performance [71].

Fig. 7 shows the different types of 500 MW power plant in amine absorption technology for power generation and abatement costs of CO₂ capture [95]. For the widely used supercritical and ultra-supercritical unites, the cost of CO₂ reduction accounts for a large part of the total cost, it is as the same as that of ammonia solution. The main problems of flue gas decarbonization technology are high energy consumption of CO₂ capture process and utilization of a large amount of CO₂ captured [96]. After improvement of process and solvent, the energy consumption of MEA method is estimated to be 0.19–0.28 MW h/t, equivalent to 20–30% of the typical plants output while it is unacceptable for plants at present [46]. After ammonia decarbonization, the solution contained a large number of NH₄HCO₃ will be decomposed thermally into ammonia and CO₂, the ammonia and the CO₂ will be recycled and collected separately. From the perspective of energy consumption, NH₄HCO₃ can be decomposed when heated to 60 °C while the MEA needs to be heated to 120 °C [97], therefore the energy consumption of the ammonia regeneration is expected to be lower than that of MEA, in other words, CO₂ capture using ammonia solution has advantages in economy. But in practice, the cost depended on many factors of system, there is no precise comparison at present. In the recent years, the SCR (selective catalytic reduction) /SNCR (selective non-catalytic reduction) and the ammonia desulfurization were applied [98,99], usage of ammonia as the common substance which also is applied in ammonia decarbonization could simplify the design, operation and maintenance, meanwhile a lot of running and management costs could be saved theoretically. Probably usage of ammonia as the common substance for removing multiple pollutions will be a direction.

Considered with the perspective of CO₂ utilization, the quantity demand of CO₂ in these fields is limited, such as chemical raw materials, food additives and secondary oil exploitation [100–104]. According to recent research, the current annual consumption of pure CO₂ is about 200 Mt/year, but compared to the total CO₂

emissions from global power plants it seems too small [2,105], as shown in Fig. 8.

Fig. 8, the market has no ability to consume such huge amount of CO₂ discharged from the coal industry at present, so the sequestration technology is essential for the disposal of excessive CO₂ [106,107]. According to the data, the cost of geological sequestration is about 0.5–5 U.S.\$/t CO₂, the cost of marine geological sequestration is about 6–12 U.S.\$/t CO₂, the cost of pipeline transportation is approximately 1–8 U.S.\$/t CO₂, the monitoring costs 0.05–0.1 U.S.\$/t CO₂ [108,109], while the possibility of cost reduction is unlikely. Except sequestration methods such as EOR, EGR, etc., there are few profitable sequestration methods. And there are few sequestration locations appropriated for power plants, which also brought additional pressure to the application of CCS in near future [110,111]. Even so, in the future sequestration technology still need to or must be developed to deal with the excessive CO₂, and the profitable CO₂ resource utilization will lay a foundation for the extend of CCS.

Considered with direct injection into the ground for permanent sequestration currently which is expensive and lacking policy supports, many people concern about energy and climate have turned to studying utilization of CO₂ [75,77]. For the companies which want to apply CO₂ emission reduction as an environmental protection technology with its high investment and low profits, optimizing the process to reduce the cost and increase the economic compensation as much as possible to make up for the huge investment is very important. Although the social appeal of carbon emission reduction is high, power enterprises in the market economic environment rarely apply it, because their decision-making is based on economic efficiency of the technology while the technology lead to the increasing cost of power generation which impacts directly on the enthusiasm of the enterprises to use carbon emission reduction [112–116]. More policy supports must be studied and applied in the start stage of carbon emission reduction.

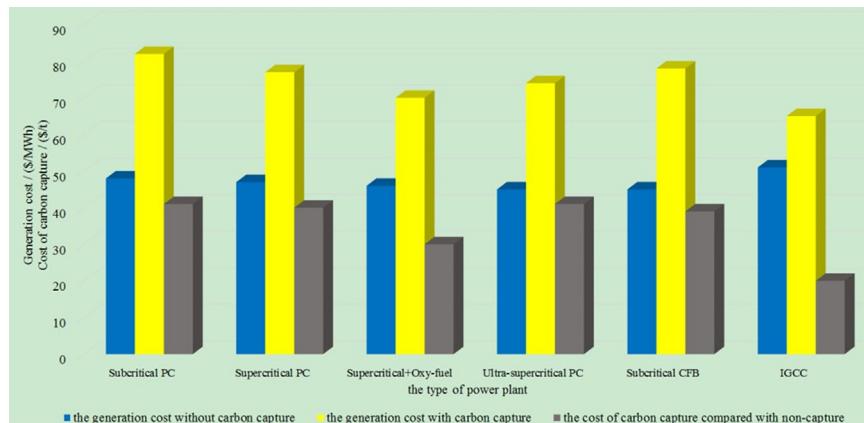


Fig. 7. The costs of power generation and CO₂ reduction.

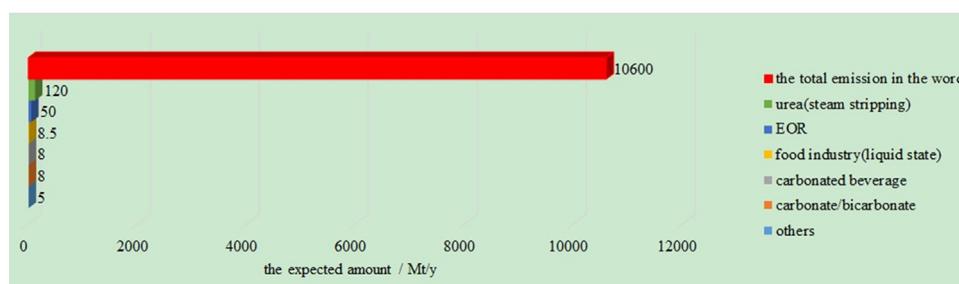


Fig. 8. The expected emission and demand of CO₂.

- A-Amine scrubbing method (2000);
- B-Advanced amine scrubbing (2005);
- C-State-of-the-art amine scrubbing method + joint removal (0–5 years);
- D-Ammonia absorption method (5–10 years);
- E-Amine-enhanced solid absorbent (10–20 years);
- F-Ammonia absorption method + by-product sales (10–30 years);
- G-Ultra-supercritical oxy-fuel combustion + Ion transport membrane (ITM) (10–30 years);
- H-Ultra-supercritical oxy-fuel combustion + ITM + joint removal (30–40 years).

According to the forecast of the National Energy Technology Laboratory (NETL) [117], along with the progress of technology, the cost of power generation using different CO_2 capture technologies will be gradually reduced, as shown in Fig. 9. The data is based on non-capture pulverized coal power plant, the cost of power generation is set to 50 \$/(MW h). After 10–30 years the plants without ultra-supercritical boiler will use the technology combined ammonia absorption method with by-product sales, the increasing rate of power generation cost can be reduced to 19%. After 30–40 years the plants with ultra-supercritical boilers will use the technology consisted of oxy-fuel combustion, ITM and joint removal technology, the increasing rate of power generation cost can be reduced to 11%. For the most of the existing plants without ultra-supercritical boiler, the minimal increasing rate of power generation cost with carbon emission reduction can be achieved by using the technology combined ammonia absorption method with by-product sales (such as Fig. 9 point F). In theory the by-products of transformed resource utilization, such as ammonium bicarbonate, sodium

bicarbonate, sodium carbonate, etc., can be sold. The profits of regenerative resource utilization and MEA method mainly come from the selling of CO_2 [118–120]. Therefore, the economic efficiency of transformed resource utilization is higher than that of regenerative utilization considered the production value. But more researches and developments about transformed resource utilization should be done firstly, especially in the transformed efficiency in power plants.

4. The prospect of CO_2 resource utilization

CO_2 resource utilization can not only reduce carbon emissions, but also generate an economic return to compensate for the cost of capture, the concept of CO_2 resource utilization has attracted more and more attention [106]. Compared to MEA decarbonization technology, whether from the promotion feasibility, or from the economic point of view, CO_2 resource path in power plants based on CO_2 capture using ammonia solution technology highlights its advantages. Flue gas CO_2 disposal in power plants using ammonia solution based on the conversion and utilization path has good prospects, this should be one of the main direction of development for carbon capture, but also more secure, more effective carbon sequestration technologies must be studied to cope with the excess CO_2 . With the current study, the main research direction for flue gas CO_2 resources in power plants are summarized, as shown in Fig. 10.

Now, studies of the reaction mechanism and control conditions have already been started, the more in-depth direction should be studied in future. Due to capture in power plants occupies the highest cost, so the present work is still concentrated in this part, aimed at reducing the capture cost which is based on the enough

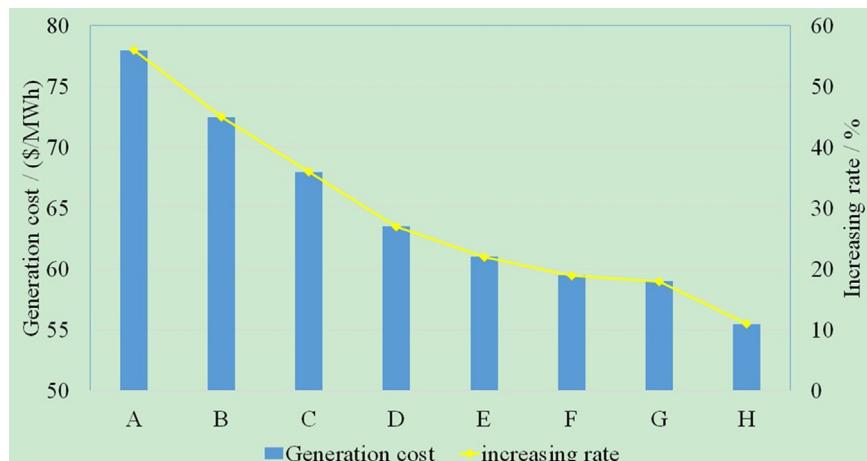


Fig. 9. Costs of pulverized coal plants applied different CO_2 reduction technologies.

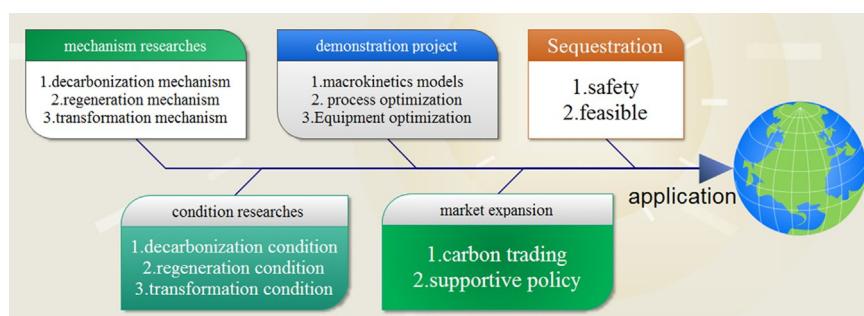


Fig. 10. The research direction of flue gas CO_2 resource utilization expected in the future.

fundamental research. But in the longer term, recycling and conversion of these two paths also need to be started, and technologies in the demonstration project should be the actual verification to improve optimization for the process and equipment design, meanwhile the optimization of the energy consumption also cannot be neglected. These problems in this regard will be solved through the optimization and adjustment in actual plant, and related policy and emerging carbon trading market should be paid more attention.

5. Conclusions

(1) With the attention of international community to the problem of CO₂, all over world is facing severe CO₂ emission reduction responsibilities. At present, due to the huge investment and technical difficulties, the sequestration technology of post-combustion carbon capture is difficult to applied widely, CO₂ resource utilization is even more appropriate.

(2) Compared with carbon transformation in the traditional chemical industry, power plant CO₂ resource utilization is influenced by many factors, such as the change of the reaction conditions, the change of the reaction course, dynamics differences in the reactor etc. Until now, reaction control conditions and energy consumption are lack of research in each stage. The key to the application of the technology is the energy consumption and the consumption of raw materials in the power plant for CO₂ conversion process which should be better than the equivalent levels in chemical plant, and the transformed products also needs to meet market required performance and price superiority.

(3) Two viable paths for CO₂ resource utilization based on carbon capture using ammonia method have been divided in the paper. One path is regenerative resource utilization; another path is transformed resource utilization. The two paths can effectively reduce the CO₂ emissions from the power plant flue gas, and can effectively use CO₂ and achieve better social and economic benefits. For the enterprises, gradually established carbon trading market, diversified products produced by transforming resources path have better market prospects than pure CO₂ gas utilization and storage. Finally the CO₂ resource utilization based on carbon capture using the ammonia method is pointed out of beneficial to the carbon emission reduction in coal-fired power plants; especially transformed resource utilization has economic advantage and good application prospects.

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References

- [1] Marcott SA, Shakun JD, Clark PU, Mix AC. A reconstruction of regional and global temperature for the past 11,300 years. *Science* 2013;339(6124):1198–1201.
- [2] International Energy Agency. CO₂ emissions from fuel combustion: 1971–2005. Sour OECD Energy 2007.
- [3] National Bureau of Statistics of China. China Statistical Yearbook. Beijing: China Statistics Press; 2006.
- [4] Bai B, Li X, Liu Y, Zhang Y. Preliminary study on CO₂ industrial point sources and their distribution in china. *Chin J Rock Mech Eng* 2006;25:2918–23.
- [5] Ciferno JP, Fout TE, Jones AP, Murphy JT. Capturing carbon from existing coal-fired power plants. *Chem Eng Prog* 2009;105(4):33.
- [6] Granite EJ, O'Brien T. Review of novel methods for carbon dioxide separation from flue and fuel gases. *Fuel Process Technol* 2005;86(14):1423–34.
- [7] Ma SC, Wang MX, Sun YX, Cui JW, Chen WZ. Efficiency Comparison of CO₂ Removal Respectively with Ammonia Solution and MEA. *J Chin Soc Power Eng* 2012;1:10.
- [8] Bai H, Yeh AC. Removal of CO₂ greenhouse gas by ammonia scrubbing. *Ind Eng Chem Res* 1997;36(6):2490–3.
- [9] Ciferno JP, DiPietro P, Tarka T. An economic scoping study for CO₂ capture using aqueous ammonia. Washington D C: US Department of Energy (DOE); 2005.
- [10] Song C. Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catal Today* 2006;115(1):2–32.
- [11] Ciferno JP, DiPietro P, Tarka T. An economic scoping study for CO₂ capture using aqueous ammonia. Final Report. Pittsburgh, PA: National Energy Technology Laboratory, US Department of Energy; 2005.
- [12] Resnik K, Garber W, Hreha D, Yeh J, Pennline H. A parametric scan for regenerative ammonia-based scrubbing for the capture of CO₂. In: Proceedings of the 23rd Annual International Pittsburgh Coal Conference, Pittsburgh, PA 2006.
- [13] Corti A, Lombardi L. Reduction of carbon dioxide emissions from a SCGT/CC by ammonia solution absorption—preliminary results. *Int J Therm* 2010;7(4):173–81.
- [14] Figueroa JD, Fout T, Plasynski S, McIlvried H, Srivastava RD. Advances in CO₂ capture technology-The US Department of Energy's Carbon Sequestration Program. *Int J Greenh Gas Con* 2008;2(1):9–20.
- [15] Huang H, Chang SG, Dorchak T. Method to regenerate ammonia for the capture of carbon dioxide. *Energy Fuel* 2002;16(4):904–10.
- [16] Yao SI, Wei L. Capture and separation of CO₂ from flue gas by coupling free and immobilized amines. *J Environ Sci* 2002;14(9):451–6.
- [17] Zhang Y, Li ZZ, Li CZ, Zhang JW, Jim Z, Li X, et al. Dual benefits of a new CO₂ sequestration technology from fossil fuel power plants. *Mod Electr Power* 2002;19(3):1–7.
- [18] Lee JW, Li R. Integration of fossil energy systems with CO₂ sequestration through NH₄HCO₃ production. *Energ Convers Manag* 2003;44(9):1535–46.
- [19] Day D, Evans RJ, Lee JW, Reicosky D. Valuable and stable carbon co-product from fossil fuel exhaust scrubbing. *Prepr Pap-Am Chem Soc, Div Fuel Chem* 2004;49(1):352.
- [20] Rao AB, Rubin ES. A technical, economic, and environmental assessment of amine-based CO₂ capture technology for power plant greenhouse gas control. *Environ Sci Technol* 2002;36(20):4467–75.
- [21] Yeh AC, Bai H. Comparison of ammonia and monoethanolamine solvents to reduce CO₂ greenhouse gas emissions. *Sci Total Environ* 1999;228(2):121–33.
- [22] Resnik KP, Yeh JT, Pennline HW. Aqua ammonia process for simultaneous removal of CO₂, SO₂ and NO_x. *Int J Environ* 2004;4(1):89–104.
- [23] Liu F, Wang SJ, Chen CH, Xu XC. Experimental research of CO₂ removal by ammonia solutions from flue gas of coal-fired power plant In: Proceedings of the 6th International Symposium on Coal Combustion, Huazhong University of Science and Technology, Wuhan, China 2007; 727–731.
- [24] Hsu Chiaha. Study on carbon dioxide removals from flue gas using chemical absorption method Taiwan: Cheng Kung University; 2003.
- [25] Ma SC, Sun YX, Zhao Y, Fang WW, Han J, Liang PZ. Experimental and mechanism research on CO₂ capture from simulating flue gas using ammonia solution. *Acta Chim Sin* 2011;69(12):1469–74.
- [26] Zhang Y, Li ZZ, Li X, Dong JX, Wang Y, Shenyang P, et al. Preliminary study to capture CO₂ in flue gas by spraying aqueous ammonia to produce NH₄HCO₃. Helminski E L. Proceedings of the second annual conference on carbon sequestration 2003 (Virginia: NETL Proceedings).
- [27] Zhang M, Sai JC, Wu SH, Li Z. Experimental study of the removal of CO₂ from coal-fired flue gas by using ammonia. *J Eng Thermal Energy Power* 2008;23(2):191.
- [28] Diao YF, Zheng XY, He BS, Chen CH, Xu XC. Experimental study on capturing CO₂ greenhouse gas by ammonia scrubbing. *Energy Convers Manag* 2004;45(13):2283–96.
- [29] Zhang J, Gong ML, Jia JX, Chen MG. Study on removal of low concentration CO₂ from flue gas by aqueous ammonia under HIGEE at normal atmosphere. *J Anhui Univ Sci Technol (Nat Sci)* 2006;26(1):48–51.
- [30] Dave N, Do T, Puxty G, Rowland R, Feron P, Attalla M. CO₂ capture by aqueous amines and aqueous ammonia: a comparison. *Energy Procedia* 2009;1(1):949–54.
- [31] Abu-Zahra MR, Schneiders LH, Niederer JP, Feron PH, Versteeg GF. CO₂ capture from power plants: part I. A parametric study of the technical performance based on monoethanolamine. *Int J Greenh Gas Con* 2007;1(1):37–46.
- [32] Liang Y. Carbon dioxide capture from flue gas using regenerable sodium-based sorbents [M.S. thesis]. Tsinghua University; 2003.
- [33] Liu F, Wang SJ, Zhang X, Sun XY, Chen CH, Xu XC. Study on ammonium bicarbonate decomposition after CO₂ sequestration by ammonia method. *Acta Sci Circumst* 2009;009:1886–90.
- [34] Zhu D, Fang M, Zhong L, Zhang C, Luo Z. Semi-batch experimental study on CO₂ absorption characteristic of aqueous ammonia. *Energy Procedia* 2011;4:156–63.
- [35] Kim JY, Han K, Chun HD. CO₂ absorption with low concentration ammonia liquor. *Energy Procedia* 2009;1(1):757–62.
- [36] Darde V, Thomsen K, van Well WJ, Stenby EH. Chilled ammonia process for CO₂ capture. *Energy Procedia* 2009;1(1):1035–42.

[37] Qin SJ, Zheng ZS, Zhang CF, Shen XY. A study on absorption rate of CO₂ into pure ammonia aqueous solutions. *J East Chin Inst Chem Technol* 1983;2:155–67.

[38] Zheng ZS, Qin SJ, Shen XY, Zhang CF. A study on absorption rates of CO₂ into low degree carbonated ammonia-water solutions. *J East China Inst Chem Technol* 1984;2:137–46.

[39] Derkx P, Versteeg G. Kinetics of absorption of carbon dioxide in aqueous ammonia solutions. *Energy Procedia* 2009;1(1):1139–46.

[40] Hatch Jr T, Pigford R. Simultaneous absorption of carbon dioxide and ammonia in water. *Ind Eng Chem Fundam* 1962;1(3):209–14.

[41] Pazuki G, Pahlevanzadeh H, MohseniAhooee A. Solubility of CO₂ in aqueous ammonia solution at low temperature. *Calphad* 2006;30(1):27–32.

[42] Qian ZK. Kinetics of carbonation process in the production of soda. *Soda Ind* 1997;1:32–7.

[43] Zeng Q, Guo Y, Niu Z, Lin W. Mass transfer coefficients for CO₂ absorption into aqueous ammonia solution using a packed column. *Ind Eng Chem Res* 2011;50(17):10168–75.

[44] Yang H, Xu Z, Fan M, Gupta R, Slimane RB, Bland AE, et al. Progress in carbon dioxide separation and capture: a review. *J Environ Sci* 2008;20(1):14–27.

[45] Liu J, Wang S, Zhao B, Tong H, Chen C. Absorption of carbon dioxide in aqueous ammonia. *Energy Procedia* 2009;1(1):933–40.

[46] Qin F, Wang S, Hartono A, Svendsen HF, Chen C. Kinetics of CO₂ absorption in aqueous ammonia solution. *Int J Greenh Gas Con* 2010;4(5):729–38.

[47] Liu J, Wang S, Qi G, Zhao B, Chen C. Kinetics and mass transfer of carbon dioxide absorption into aqueous ammonia. *Energy Procedia* 2011;4:525–32.

[48] Riahi K, Rubin ES, Taylor MR, Schrattenholzer L, Hounshell D. Technological learning for carbon capture and sequestration technologies. *Energy Econ* 2004;26(4):539–64.

[49] Li X, Hagaman E, Tsouris C, Lee JW. Removal of carbon dioxide from flue gas by ammonia carbonation in the gas phase. *Energ Fuel* 2003;17(1):69–74.

[50] Ma SC, Sun YX, Cui JW, Zhao Y. Experiment and analysis of ammonia escape from decarburization absorbent inhibited by NHD. *CIESC J* 2011;62(5):1408–13.

[51] Pellegrini G, Strube R, Manfrida G. Comparative study of chemical absorbents in post combustion CO₂ capture. *Energy* 2010;35:851–7.

[52] You JK, Park HS, Yang SH, Hong WH, Shin W, Kang JK, et al. Influence of additives including amine and hydroxyl groups on aqueous ammonia absorbent for CO₂ capture. *J Phys Chem* 2008;112:4324–7.

[53] Ma SC, Song HH, Zang B, Chen GD. Experimental study on additives inhibiting ammonia escape in carbon capture process using ammonia method. *Chem Eng Res Des* 2013;91(12):2775–81.

[54] Seo JB, Jeon SB, Kim JY, Lee GW, Jung JH, Oh KJ. Vaporization reduction characteristics of aqueous ammonia solutions by the addition of ethylene glycol, glycerol and glycine to the CO₂ absorption process. *J Environ Sci* 2012;24:494–8.

[55] Mani F, Peruzzini M, Barzaghi F. The role of zinc(II) in the absorption-desorption of CO₂ by aqueous NH₃, a potentially cost-effective method for CO₂ capture and recycling. *Chem Sus Chem* 2008;1:228–35.

[56] Kim Y, Lim SR, Park JM. The effects of Cu(II) ion as an additive on NH₃ loss and CO₂ absorption in ammonia-based CO₂ capture process. *Chem Eng J* 2012;211:327–35.

[57] Ma SC, Song HH, Zang B, Chen GD. Experimental study of Co(II) additive on ammonia escape in carbon capture using renewable ammonia. *Chem Eng J* 2103; 234: 430–436.

[58] Hamada H, Haneda M. A review of selective catalytic reduction of nitrogen oxides with hydrogen and carbon monoxide. *Appl Catal A: Gen* 2012;421:1–13.

[59] Hu Y, Griffiths K, Norton PR. Surface science studies of selective catalytic reduction of NO: progress in the last ten years. *Surf Sci* 2009;603(10):1740–50.

[60] Yeh JT, Resnik KP, Rygle K, Pennline HW. Semi-batch absorption and regeneration studies for CO₂ capture by aqueous ammonia. *Fuel Process Technol* 2005;86(14):1533–46.

[61] Mani F, Peruzzini M, Stoppioni P. CO₂ absorption by aqueous NH₃ solutions: speciation of ammonium carbamate, bicarbonate and carbonate by a ¹³C NMR study. *Green Chem* 2006;8(11):995–1000.

[62] McLaren CR, Duncan JL. Testing of ammonia based CO₂ capture with multi-pollutant control technology. *Energy Procedia* 2009;1(1):1027–34.

[63] Rochelle GT. Amine scrubbing for CO₂ capture. *Science* 2009;325(5948):1652–4.

[64] Gao ZW, Xiao LF, Chen J, Xia C. Recent advances in the synthesis of cyclic carbonates from carbon dioxide and epoxides. *Chin J Catal* 2008;29(9):831–8.

[65] Centi G, Perathoner S. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catal Today* 2009;148(3):191–205.

[66] Zangeneh FT, Sahebdelfar S, Ravanchi MT. Conversion of carbon dioxide to valuable petrochemicals: an approach to clean development mechanism. *J Nat Gas Chem* 2011;20(3):219–31.

[67] deConinck H, Bäckstrand K. An International relations perspective on the global politics of carbon dioxide capture and storage. *Global Environ Chang* 2011;21(2):368–78.

[68] Dahowski R, Li X, Davidson C, Wei N, Dooley J, Gentile R. A preliminary cost curve assessment of carbon dioxide capture and storage potential in China. *Energy Procedia* 2009;1(1):2849–56.

[69] Plasynski S, Litynski J, McIlvried H, Srivastava R. Progress and new developments in carbon capture and storage. *Crit Rev Plant Sci* 2009;28(3):123–38.

[70] Buller AT, Kårstad O, De Koeijer G. Carbon dioxide-capture, storage and utilization. *Statoil Res Technol Memoir* 2004(5):.

[71] Grünwald R. A review of carbon dioxide capture and storage-technology, potentials, risks, costs, and regulation. *Gaia* 2009;18:211–20.

[72] Bachu S. CO₂ storage in geological media: Role, means, status and barriers to deployment. *Prog Energ Combust* 2008;34(2):254–73.

[73] Dahowski R, Li X, Davidson C, Wei N, Dooley J. Regional opportunities for carbon dioxide capture and storage in China. A comprehensive CO₂ storage cost curve and analysis of the potential for large scale carbon dioxide capture and storage in the people's Republic of China Prepared for the US Department of Energy PNNL-19091 2009;1–85.

[74] Singleton G, Herzog H, Ansolabehere S. Public risk perspectives on the geologic storage of carbon dioxide. *Int J Greenh Gas Con* 2009;3(1):100–7.

[75] Hunt AJ, Sin EH, Marriott R, Clark JH. Generation, capture, and utilization of industrial carbon dioxide. *Chem Sus Chem* 2010;3(3):306–22.

[76] Orr Jr FM. CO₂ capture and storage: are we ready? *Energy Environ Sci* 2009;2(5):449–58.

[77] Herzog HJ, Drake EM, Adams EE. CO₂ Capture, Reuse, and Storage Technologies for Mitigating Global Climate Change: A White Paper, Final Report. Energy Laboratory, Massachusetts Institute of Technology; 1997.

[78] Ma SC, Wang MX, Meng YN, Chen WZ, Lu DL, Han TT. Research on the absorption of CO₂ from flue gas and the desorption of decarbonization solution using ammonia method. *Chem Ind Eng Pro* 2012;31(005):1143–8.

[79] Holloway S. Carbon dioxide capture and geological storage. *Phil Trans R Soc A* 2007;365(1853):1095–107.

[80] Xie HP, Xie LZ, Wang YF, Zhu JH, Liang B, Ju Y. CCU: A more feasible and economic strategy than CCS for reducing CO₂ emissions. *J Sichuan Univ: Eng Sci Ed* 2012;44:1–5.

[81] Liu HH. Carbon geological sequestration: LBNL's research activities. US: Lawrence Berkeley National Laboratory; 2012.

[82] Solomon S, Carpenter M, Flach TA. Intermediate storage of carbon dioxide in geological formations: a technical perspective. *Int J Greenh Gas Con* 2008;2(4):502–10.

[83] Balat M, Balat H, Öz C. Applications of carbon dioxide capture and storage technologies in reducing emissions from fossil-fired power plants. *Energy Sour, Part A* 2009;31(16):1473–86.

[84] Monea M, Knudsen R, Worth K, Chalaturnyk R, White D, Wilson M, et al. Considerations for monitoring, verification, and accounting for geologic storage of CO₂. *Geophys Monogr Ser* 2009;183:303–16.

[85] Shuwei L, Chuan W, Wenyang T, Yong L, Bo P. Hou's Process (for soda manufacture) and Sichuan Chemical Industry to Commemorate Doc HouDebang's 120th Birthday. 1. Sichuan Chemical Industry; 2011; 16.

[86] Zhuang Q, Clements B, Li Y. From ammonium bicarbonate fertilizer production process to power plant CO₂ capture. *Int J Greenh Gas Con* 2012;10:56–63.

[87] Zhang ZM, Feng YQ. New Nitrogenous Fertilizer: Long-Effect Ammonium Bicarbonate. Chemical Industry Press; 2000; 84–101.

[88] Zheng XY. Experimental study on SO₂ and CO₂ recovery from flue gases by ammonia. Beijing: Tsinghua University; 2002.

[89] Liu F, Wang S, Chen C, Xu X. Research progress of CO₂ capture by using ammonia from flue gas of power plant [J]. *J Chem Ind Eng Soc Chin* 2009;60(2):269–78.

[90] Erisman JW, Sutton MA, Galloway J, Klimont Z, Winiwarter W. How a century of ammonia synthesis changed the world. *Nat Geosci* 2008;1(10):636–9.

[91] Liao X, Liu F, Huang J. Study on production of sodium carbonate from ammonium bicarbonate and sodium chloride. *Chin J Appl Chem* 1989;3:26–30.

[92] Shen HM. Technology concerning low carbon economics and CO₂ exhaustion reduction from chemical fertilizer production. *Chem Fertil Des* 2010;4:1.

[93] Xiao XL, Li JM, Duan CL, Lin ZW. Production of urea by agricultural ammonium bicarbonate. *China Patent* 92108006. 1993-06-30.

[94] Damiani D, Litynski JT, McIlvried HG, Vikara DM, Srivastava RD. The US department of Energy's R&D program to reduce greenhouse gas emissions through beneficial uses of carbon dioxide. *Greenh Gas: Sci Technol* 2012;2(1):9–16.

[95] Deurch J, Moniz E. The Future of Coal. Cambridge, MA: MIT Laboratory for Energy and the Environment; 2006.

[96] Azar C, Lindgren K, Larson E, Mollersten K. Carbon capture and storage from fossil fuels and biomass—costs and potential role in stabilizing the atmosphere. *Clim Change* 2006;74(1–3):47–79.

[97] Shale C, Simpson D, Lewis P. Removal of sulfur and nitrogen oxides from stack gases by ammonia. *Chem Eng Prog Symp Ser* 1971;67(115):52–7.

[98] Blakeman PG, Twigg MV, Walker A.P., et al. Selective Catalytic Reduction: U.S. Patent 7,264,785. 2007-9-4.

[99] Muzio L, Quartuccy G, Cichanowicz J. Overview and status of post-combustion NO_x control: SNCR, SCR and hybrid technologies. *Int J Environ Pollut* 2002;17(1):4–30.

[100] Zhou JH, Gan Y, Pu Y, Ning P. Application of ammonia process flue gas desulphurization to coal-fired boiler. *Environ Eng* 2005;3:15.

[101] Liu DY, Zhu CQ, Xu CX. Application of ammonia process of flue gas desulfurization in petrochemical thermoelectricity plant. *China Environ Protect Ind* 2008;11:10.

[102] Yu KMK, Curcic I, Gabriel J, Tsang SCE. Recent advances in CO₂ capture and utilization. *Chem Sus Chem* 2008;1(11):893–9.

[103] Omae I. Aspects of carbon dioxide utilization. *Catal Today* 2006;115(1):33–52.

[104] Al-Saleh Y, Vidican G, Natarajan L, Theeyattuparampil V. Carbon capture, utilisation and storage scenarios for the Gulf Cooperation Council region: a Delphi-based foresight study. *Futures* 2012;44(1):105–15.

[105] Global CCS Institute, Accelerating the uptake of CCS: industrial use of captured carbon dioxide. Available from: www.globalccsinstitute.com. 2011;724.

[106] Liu H, Gallagher KS. Driving carbon capture and storage forward in China. *Energy Procedia* 2009;1(1):3877–84.

[107] Beck B, Surridge T, Liebenberg J, Gilder A. The current status of CCS development in South Africa. *Energy Procedia* 2011;4:6157–62.

[108] Rubin E, de Coninck H. IPCC special report on carbon dioxide capture and storage, UK: Cambridge University Press TNO; 2004; 2 (Cost Curves for CO₂ Storage, Part 2005).

[109] Rubin ES, Chen C, Rao AB. Cost and performance of fossil fuel power plants with CO₂ capture and storage. *Energ Policy* 2007;35(9):4444–54.

[110] Friedmann SJ, Dooley JJ, Held H, Edenhofer O. The low cost of geological assessment for underground CO₂ storage: Policy and economic implications. *Energy Convers Manage* 2006;47(13):1894–901.

[111] Shackley S, Gough C. Carbon Capture and Its Storage: An Integrated Assessment. Ashgate Publishing, Ltd.; 2006.

[112] de Best-Waldhoer M, Daamen D, Faaij A. Informed and uninformed public opinions on CO₂ capture and storage technologies in the Netherlands. *Int J Greenh Gas Con* 2009;3(3):322–32.

[113] Curry TE, Reiner D, Ansolabehere S, Herzog H. How aware is the public of carbon capture and storage? US: MIT; 2005.

[114] Baker ED, Chon H, Keisler JM. Carbon capture and storage: combining economic analysis with expert elicitation to inform climate policy. *Clim Change* 2009;96(3):379–408.

[115] Davison J. Performance and costs of power plants with capture and storage of CO₂. *Energy* 2007;32(7):1163–76.

[116] Oldenburg CM. Why we need the 'and' in 'CO₂ utilization and storage'. *Greenh Gas: Sci Technol* 2012;2(1):1–2.

[117] David J, Herzog H. The cost of carbon capture. *Proceedings of the Fifth International Conference on Greenhouse Gas Control Technologies* 2000:985–90 (Cairns, Australia).

[118] Al-Juaied M, Whitmore A. Realistic costs of carbon capture, Discussion Paper. Belfer Center Sci Int Aff 2009:8.

[119] Davison J, Thambimuthu K. An overview of technologies and costs of carbon dioxide capture in power generation. *Proc Inst Mech Eng Part A J Power Eng* 2009;223(3):201–12.

[120] Thambimuthu K, Davison J, Gupta M. CO₂ capture and reuse. In: *Proceedings of the IPCC workshop on carbon dioxide capture and storage* 2002;31–52.